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(54) Temporary aqueous coating composition

(57) A coating composition for providing temporary (expecially protective) coatings on surfaces (especially the hydrophobic paintwork of newly finished motor vehicles) comprises a particulate copolymer dispersed in water containing less than 10 wt% of volatile organic solvent. The particulate copolymer comprises 7 to 20 wt% acrylic or methacrylic acid, 0.5 to 10 wt% methacrylamide, 1 to 10 wt% of an oligomer comprising a long-chain hydrophilic moiety of molecular weight 500 to 4000 and a hydrophobic moiety (e.g. methoxy PEG methacrylate), and other monomers such as methyl methacrylate and butyl acrylate.

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TEMPORARY AQUEOUS COATING COMPOSITION

This invention relates to a temporary aqueous coating composition, especially a protective composition for use on hydrophobic surfaces such as for example plastics or painted surfaces and in particular the painted surfaces found on newly manufactured motor vehicles or marine craft.

Newly manufactured motor vehicles are usually provided with a temporary protective coating to reduce the risk of damage to their paintwork during storage and delivery. The protective coating is subsequently removed before the final delivery of the vehicle to a customer. A good temporary coating composition should be environmentally acceptable yet preferably able to wet a highly hydrophobic surface such as paint thoroughly so that when it dries, it produces a coating which is tenacious and essentially continuous. A temporary protective coating should be

thick enough to protect for example paint and all temporary coatings should be thin enough to be easily removed even after storage for long periods in a warm climate. Removal of the coating should also produce an environmentally acceptable effluent. In addition, a temporary protective coating should also resist removal by non-alkaline water (especially rain). It should also resist dirt, be highly transparent and colourless (unless colour is deliberately required) and the transparency and colourlessness should not be badly affected by rain.

For many years, hydrocarbon wax has been used to provide temporary coatings (and in particular protective coatings) on newly painted vehicles. Generally the wax is first dissolved in a volatile organic solvent and the solution is sprayed onto the (usually) hydrophobic surface where the solvent evaporates leaving a wax coating which may be quite thick if required. However the amount of solvent which needs to be used is increasingly environmentally unacceptable and the wax coatings obtained are at best only translucent and they pick up dirt easily. Moreover, when first applied the wax coatings are undesirably easily removable by even light abrasion yet during ageing (especially in warm climates) they become tenacious and their removal then needs the use of pressurised jets of hot water mixed with volatile organic solvent. Temperatures of 70°C and pressures of 100 bar are widely used. It is not only inconvenient to have to use such jets, but their solvent content is again environmentally undesirable and the water, solvent and removed wax combine to produce an environmentally unacceptable effluent.

The need to reduce the amount of organic solvent associated with temporary coatings has led to recent attempts to use aqueous coating compositions comprising particles of hydrocarbon wax dispersed in water with the aid of surfactants. Such compositions still only produce translucent coatings which require inconvenient methods for removal (for example pressure jets or buffing techniques) and still produce environmentally unacceptable effluents when they are removed. In addition two new problems arise. Firstly the coatings obtained have an undesirably high sensitivity to rain. Secondly, the coating compositions have only a moderate ability to wet hydrophobic surfaces which means that they are intolerant of even slightly dirty painted surfaces and so can only be safely applied to surfaces which are ultra clean.

European patent EP 0 115 694B discloses an attempt to overcome the problems associated with wax by using coating compositions comprising sterically stabilised particles of a copolymer comprising various carboxylic acids including methacrylic acid and either esters, nitriles or amides of acrylic or methacrylic acids instead of the wax. The coating compositions were found to have a good ability to wet hydrophobic surfaces and they produced highly transparent colourless tenacious coatings which had a good resistance to rain yet could easily be removed by washing with conventional dilute alkaline (pH 9 to 12.5) aqueous solutions free from volatile organic solvents to produce effluents which were acceptable for disposal down the local water authority drains. EP 0 115 694B discloses that its coating compositions contain volatile organic solvent (butanol and

methylated spirit which is essentially ethanol) and unfortunately it has been found that the compositions must contain in excess of 20 wt% (and usually over 25 wt%) of the solvent otherwise a viscous precipitate of dissolved copolymer forms which prevents application of the coating composition by any practicable techniques. Coating compositions containing more than 10 wt of volatile organic solvent , contravene new legislation concerning temporary protective coatings and in practice many users insist that new coating compositions contain less than 5 wt% volatile organic solvent. Therefore whilst the disclosure of EP 0 115 694B solves many of the problems associated with wax coating, it fails to produce an environmentally acceptable system.

British patent specification GB 2 158 831A discloses an attempt to reduce the problem of polymer precipitation met with by the compositions of EP 0 115 694B. To do this, GB 2 158 831A employs a fully soluble copolymer made by the free radical initiated solution copolymerisation of for example methyl methacrylate, butyl acrylate, methacrylic acid and methacrylamide in organic solvent to produce a solution of copolymer fully soluble in organic solvent. This solution is then treated with enough aqueous ammonia to neutralise all the methacrylic acid groups so rendering the copolymer soluble in certain mixtures of water and organic solvent. Further water is added to the system to produce an aqueous coating composition comprising the ammonium salt of the copolymer fully dissolved in the mixture of water and organic solvent. However it has been found that the compositions made according to GB 2 158 831A cannot tolerate a reduction in their organic

solvent contents of below about 15 wt% for otherwise the copolymer precipitates forming an undispersed residue which cannot be realistically applied to a surface. Hence GB 2 158 831A also fails to produce an environmentally acceptable system.

An object of this invention is to provide a more environmentally acceptable aqueous coating composition containing less than 10 wt% of volatile organic solvent which can be used to produce a temporary coating.

Accordingly this invention provides an aqueous coating composition suitable for use in the application of temporary (especially protective) coatings which composition comprises water and a dispersion of particulate water-insoluble copolymer which has a Tg (glass transition temperature) of from 5 to 60°C (preferably 20 to 45°C) and comprises

i) from 7 to 20 wt% of copolymerised acrylic or methacrylic acid or a mixture of the two,

ii) from 0.5 to 10 (preferably 2 to 7) wt% of copolymerised methacrylamide

iii) from 1 to 10 wt% based on the weight of the particulate copolymer of an oligomer comprising a long chain hydrophilic moiety which moiety has a molecular weight of from 500 to 4000 and a hydrophobic moiety chemically bonded to the particulate copolymer and

iv) the balance being copolymerised monomers of the type copolymerisable with acrylic or methacrylic acid and methacrylamide,

the percentages being based on the total weight of the particulate copolymer and wherein the composition comprises from 0 to 10 wt% (preferably 0 to 5 wt% and usually 0.1 to 2 wt%) of organic solvent, the percentage being based on the combined weights of water, organic solvent and particulate copolymer in the composition.

Even though the coating compositions of this invention contain less than 10 wt% of organic solvent, they do not suffer unwanted precipitations at ambient temperatures (for example 15°C) and when applied to a surface and allowed to dry they produce abrasion resistant tenacious coatings even when the surface is highly hydrophobic. The coatings are also transparent and colourless (unless a deliberate choice is made to colour the coating), resistant to rain and the pick-up of dirt, and removable by gentle washing with dilute alkaline aqueous solutions to produce an environmentally acceptable effluent. The coatings can be from 3 to 100 μm thick preferably from 3 to 50 μm thick and 5 to 10 μm thick where ease of removal is especially important. 1μm is 10^{-6}m.

Organic solvent generally serves to enhance coalescence of the particulate copolymer and may help the coating composition to wet a surface. The organic solvent usually has a boiling point at 1 bar of below 300°C and preferably from 60 to 150°C. Most commonly used materials are alcoholic in nature such as aliphatic alcohols and preferably ethylene glycol monohexyl (or monobutyl) ether or di-ethyleneglycol.

At least some of the chemically bonded oligomer

functions as a steric stabiliser and serves to maintain the particulate copolymer dispersed in the aqueous compostion until the coating composition has been applied to a surface and begins to dry. Sufficient bonded oligomer should be present for this purpose. The long chain hydrophilic moiety of the oligomer may conveniently be a moiety of the type found in commercially available non-ionic surfactants such as those reviewed in Volume 22 of the third edition of Kirk-Othmer's "Encyclopaedia of Chemical Technology" published in 1983 by John Wiley of New York, see pages 360 to 377 the contents of which are herein incorporated by reference. Preferably the hydrophilic moieties comprises polyoxyethylene or polyethylene glycol chains.

Preferably the hydrophobic moieties comprise unsaturated carboxylates, especially acrylate or methacrylate which can bond to the particulate copolymer by copolymerisation during formation of the copolymer. A particularly preferred oligomer is methoxy polyethylene glycol methacrylate having a number average molecular weight of from 1500 to 3000. Alternatively the hydrophobic moiety may be a moiety such as linseed oil fatty acid which bonds to the particulate copolymer by hydrogen abstraction.

The amount of oligomer needed can sometimes be reduced if the coating composition also contains from 2 to 10 wt% (based on the weight of water, organic solvent and particulate copolymer) of a non-copolymerisable non-ionic surfactant. For example the composition may contain alkyl phenol ethoxylates containing from 10 to 40 ethylene oxide units in each hydrophilic chain such as the commercially available adducts of nonyl phenol and

ethylene oxide. The non-ionic surfactants are reviewed in Kirk-Othmer ibid.

Preferably the number average particle size of the particles of copolymer in the composition when measured using photon correlation spectroscopy should be from 0.05 to 2μm.

It has been found that a good compromise between ease of removal of the coating from a substrate and good resistance to pick-up of dirt can be achieved if the Tg of the particulate copolymer is from 20 to 45°C. Tg (i.e. glass transition temperature) is measured by power compensation differential scanning calorimetry as described on pages 4 to 9 of the book "Thermal Characteristics of Polymeric Materials" edited by E A Turi and published in 1981 by Academic Press INC (London) Ltd, the contents of which pages are herein incorporated by reference. The calorimetry should be performed on samples which have been heated isothermally at 100°C for 15 minutes. Preferably the copolymer has a weight average molecular weight (when determined by gel permeation chromatography against a polystyrene standard) of 15,000 to 200,000 and usually the molecular weight will be from 15,000 to 50,000.

Illustrative of monomers which conveniently undergo free radical initiated copolymerisation with acrylic or methacrylic acids and methacrylamide are C_1 to C_{12} alkyl esters of unsaturated aliphatic carboxylic acids such as the methyl, ethyl, butyl, iso-butyl, 2-ethyl hexyl or lauryl esters of acrylic or methacrylic acids, vinyl esters of aliphatic acids such as vinyl acetate or vinyl versatate and vinyl aromatics such as styrene and vinyl toluene. Hydrophilic monomers such as hydroxy ethyl acrylate or methacrylate should only be used in amounts

which do not confer any significant water solubility on the particulate copolymer. The preferred copolymerisable monomers are methyl methacrylate and butyl acrylate which are preferably present in the copolymer in a weight ratio of from 0.5 to 1.2:1. Copolymers used in this invention can be conveniently made by a copolymerisation process performed in water usually containing non-ionic surfactant. The acrylic and/or methacrylic acid, methacrylamide and copolymerisable oligomer are dissolved in the water whereas co-monomers such as methyl methacrylate and butyl acrylate which are only sparingly soluble in water are dispersed in the water as an emulsion by means of the surfactant. Copolymerisation is preferably initiated by a redox system such as L-ascorbic acid and hydrogen peroxide. Molecular weight may be modified by the use of conventional chain transfer agents such as mercaptans. An important advantage arising from the use of copolymerisation processes of this type is that very little water-soluble copolymer by-product is produced and as a result the compositions of this invention may comprise only 0 to 5 wt% (usually 0.1 to 3 wt%) of water-soluble copolymer based on the combined weight of water, particulate copolymer and water soluble copolymer. Also the water-soluble copolymer will contain larger amounts of copolymerised acid and so the water-soluble copolymer can easily comprise at least 30 wt% (and usually 40 to 70 wt%) of copolymerised acrylic and/or methacrylic acid with the balance being copolymerised monomers of the type

copolymerisable with acrylic and/or methacrylic acid. The percentages are based on the weight of the water soluble copolymer.

A more uniform particle size distribution can be obtained if the copolymerisation is preceded by a short pre-polymerisation in which one or more sparingly soluble co-monomers are polymerised in the absence of acid and amide. The pre-polymerisation produces polymer or copolymer seeds onto which the products of the main copolymerisation can form. Preferably from 5 to 15 wt% of the particulate copolymer should be formed during the pre-polymerisation.

The copolymerisation process generally produces a precursor for the coating composition which precursor is subsequently adjusted by for example the addition of more water and/or volatile organic solvent. The composition may also contain various other ingredients used conventionally in aqueous coating compositions such as thickeners, auxiliary ionic surfactants, light stabilisers, corrosion inhibitors, antifoaming agents, pigments (if a coloured ocating is wanted) and compounds known as "builders" to the detergent trade and which promote the action of surfactants. If desirable, some water may be removed to produce a concentrate which is cheaper to transport but which can be converted to a coating composition by making the adjustments described above. Preferably a coating composition comprises from 5 to 30 wt% of solid material (based on the total weight of the coating composition but exclusive of any pigment). However, application is usually easier if the composition comprises from 10 to 20 wt% of solid material (exclusive of pigment). A concentrate may contain from 30 to 50 wt% of solid material again exclusive of any pigment.

The invention further provides a method for providing a temporary coating on a surface which method comprises applying (usually spraying) a temporary aqueous coating composition according to this invention onto the surface to provide a coating on the surface preferably in an amount such that when the coating dries it has a thickness of from 3 to 40 (preferably 5 to 10) μm (1μm is 10^{-6}m).

The invention is further illustrated by the following Examples.

EXAMPLE 1

This Example illustrates the preparation of a precursor dispersion for use in the preparation of a temporary coating composition according to this invention.

Firstly a seed copolymer was formed by adding a mixture consisting of methyl methacrylate, butyl acrylate and p-octyl mercaptan (in amounts shown in Table 1) to 364g of de-ionised water containing 5.9g of a simple non-copolymerisable non-ionic surfactant which was the adduct of nonyl phenol and ethylene oxide available from Imperial Chemical Industries PLC under the trade name "Synperonic" NP20/80.

TABLE 1

Example	Methyl Methacrylate g	Butyl Acrylate g	*p-octyl Mercaptan g
1	20	25	0.5

* chain transfer agent.

After completion of the addition, the mixture obtained was stirred at 40°C for 15 minutes under nitrogen. Then a solution of 0.15g L-ascorbic acid in 7g de-ionised water and a solution of 1.4g of 20 volume hydrogen peroxide in 7g of de-ionised water were added to the stirred mixture as a redox initiator. The mixture was maintained at 40°C and stirred for a further 60 minutes. A water insoluble seed copolymer of methyl methacrylate and butyl acrylate was formed which existed as a dispersion of fine particles. This dispersion of seed copolymer was maintained at 40°C and used to produce the precursor dispersion as follows:

A copolymerisation mixture was made by

a) dissolving methacrylic acid and methacrylamide

and

b) dispersing methyl methacrylate, butyl acrylate and p-octyl mercaptan to form an emulsion

(all in amounts shown in Table 2) in 308g of de-ionised water containing 25g of "Synperonic" NP 20/80 and 39g of methoxy polyethylene glycol (number average molecular weight 2000) methacrylate dissolved in 39g of a 3:1 mixture of deionised water and propylene glycol. The copolymerisation mixture

TABLE 2

Example	Methyl Meth-acrylate g	Butyl Acry-late g	Meth-acrylic Acid g	Meth-acryl-amide g	p-octyl Mercaptan g
1	170	209	50	25	4.8

was then added to the dispersion of seed polymer over a period of 200 minutes together with a solution of 1.4g of L-ascorbic acid in 98.6g of de-ionised water and a solution of 14.3g of 20 volume hydrogen peroxide in 85.7g de-ionised water which together form a redox initiator system. During the addition the dispersion was maintained at 40°C under nitrogen and was stirred continually. Heating and stirring under nitrogen were continued for a further 60 minutes after addition of the emulsion had been completed. A dispersion of a water insoluble particulate copolymer of methyl methacrylate, butyl acrylate, methacrylic acid, methacrylamide and copolymerised surfactant was obtained. The dispersion also contained from 2 to 3 wt% of a dissolved copolymer of these co-monomers containing about 50 wt% of copolymerised methacrylic acid. The dispersion was suitable for use as a precursor for a

coating composition according to this invention. The particulate copolymer had a Tg of 23°C and a weight average molecular weight of about 4000. The dispersion contained 36.5 wt% of solid material and the particles of copolymer in the dispersion had an average particle size of about 0.1µm.

EXAMPLES 2 AND 3

These Examples illustrate the use of the precursor of Example 1 in the making of a coating composition according to this invention.

41.1g of the dispersion of copolymer made according to Example 1 was mixed with 58.9g of either Mixture a (Example 2) or Mixture b (Example 3) below. Mixing was performed by adding both components to a mixing vessel and stirring for 5 minutes.

Mixture a		Mixture b	
860g	de-ionised water	784g	de-ionised water
278g	*"Synperonic" NP8	278g	*"Primal" RM8
20g	*"Primal" RM8	100g	*FC 135
20g	*Hexyl "Cellosolve"	16g	*Hexyl Cellosolve

* "Synperonic" NP8 is an alternative adduct of nonyl phenol and ethylene oxide available from Imperial Chemical Industries PLC

* "Primal" RM8 is an associative thickener supplied by Rohm and Haas.

* FC 135 is a fluorinated quaternary ammonium cationic surfactant supplied by the 3M Company.

* Hexyl "Cellosolve" is ethylene glycol monohexyl ether.

The weight percentage of volatile organic material in the compositions made according to both Example 2 and Example 3 was only 1.2 wt % yet both could be applied to the paintwork of a newly manufactured motor car to produce an essentially continuous protective coating.

EXAMPLES 4 AND 5

The Examples illustrate the use of the coating compositions made according to Examples 2 and 3.

Coating compositions made according to Examples 2 and 3 were each in turn fed to a conventional spray gun of the type used in providing temporary protective coatings on motor cars and set for use with low viscosity liquids. The compositions were sprayed at ambient temperature (15 to 20°C) onto the hydrophobic paintwork of a newly manufactured motor car where they wetted the surface and produced a coating which when it had dried had a thickness of from 5 to 10μm. Such coatings provide tenacious abrasion resistant protection for the paint yet can be easily removed to produce environmentally acceptable effluent by one application of a alkaline aqueous solution of pH 10 to 12.5 such as "Remover" UL 6000 supplied by Hanson-Loran Chemical Company Incorporated (pH 10) or such as the removing fluid sold by Imperial Chemical Industries PLC under the trade names "Belpro" 70 or "Tempro" 70 (pH 12.3). Removal is possible even after the protected vehicle has been kept for long periods in a hot climate. The coating was highly transparent and colourless, was scarcely affected by rain water and was very resistant to picking up dirt. It has also been

discovered that the coating composition is tolerant of neutralisation by alkali especially aqueous ammonia or sodium compounds and so if required (for example to minimise the risk of corrosion of metal work) the pH of the compositions can be raised, for example to 7 or even up to 10.

CLAIMS

1. An aqueous coating composition suitable for use in the application of temporary coatings which composition comprises water and a dispersion of particles of water-insoluble copolymer which particulate copolymer has a Tg (glass transition temperature) of from 5 to 60°C and comprises

i) from 7 to 20 wt% of copolymerised acrylic or methacrylic acid or a mixture of the two,

ii) from 0.5 to 10 wt% of copolymerised methyacrylamide,

iii) from 1 to 10 wt% (based on the weight of the particulate copolymer) of an oligomer comprising a long chain hydrophilic moiety which moiety has a molecular weight of from 500 to 4000 and a hydrophobic moiety chemically bonded to the particulate copolymer and

iv) the balance being copolymerised monomers of the type copolymerisable with acrylic or methacrylic acid and methacrylamide,

the percentages being based on the total weight of the particulate copolymer and wherein the composition comprises from 0 to 10 wt% organic solvent based on the combined weights of water, organic solvent and particulate copolymer in the composition.

2. A composition according to Claim 1 wherein the composition comprises from 0.1 to 5 wt% of organic solvent.

3. A composition according to Claim 1 or Claim 2 wherein the hydrophobic moiety of the oligomer is a copolymerised unsaturated carboxylic ester moiety.

4. A composition according to Claim 3 wherein the copolymerised ester moiety is acrylate or methacrylate.

5. A composition according to any one of the preceding Claims wherein the composition also comprises non-polymerisable non-ionic surfactant.

6. A composition according to any one of the preceding Claims wherein the number average particle size of the particulate copolymer is from 0.05 to 2μm.

7. A composition according to any one of the preceding Claims wherein the particulate copolymer has a molecular weight of from 15,000 to 200,000.

8. A composition according to any one of the preceding Claims wherein the particulate copolymer comprises at least one copolymerised monomer chosen from C_1 to C_{12} alkyl esters of unsaturated aliphatic carboxylic acids, vinyl esters of aliphatic acids and vinyl aromatic compounds.

9. A composition according to any one of the preceding Claims wherein the particulate copolymer comprises copolymerised methyl methacrylate, butyl acrylate and methacrylic acid.

10. A composition according to any one of the preceding Claims comprising copolymers wherein the copolymers have been made by a copolymerisation process performed in water in which the acid and amide monomers are dissolved and sparingly soluble monomers are dispersed as an emulsion.

11. A composition according to Claim 11 wherein the copolymerisation is preceded by a pre-polymerisation process performed in water of one or more monomers which are only sparingly soluble in water.

12. A composition according to any one of the preceding Claims wherein the composition comprises from 5 to 30 wt% of solid material exclusive of any pigment.

13. A composition according to Claim 13 in concentrated form wherein the concentrate comprises from 30 to 50 wt% of solid material exclusive of any pigment.

14. A composition according to any one of the preceding Claims when neutralised by the presence of ammonia ions so as to have a pH of at least 7.

15. A method for providing a temporary coating on a surface which method comprises applying a temporary aqueous coating composition according to this invention to the surface to provide a coating on the surface in an amount such that when the coating dries it has a thickness of from 3 to 40μm.

16. A method according to Claim 15 wherein the coating composition is applied by spraying.

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